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THE ASSOCIATION THEORY OF SOLUTIONS.

BY WILLIAM FRANCIS MAGIE.

(Read April 19, 1907.)

When it was discovered, by van't Hoff, that the osmotic pressure of solutions obeys the laws of gases, the conclusion was drawn, in many quarters, that the osmotic pressure is to be explained as a pressure arising from the impacts of the dissolved molecules or ions against the bounding surface of the solution, and that the part played by the solvent is simply that of a medium in which the solute is suspended, or in which it assumes a state practically equivalent to that of a gas. This conclusion was not received without opposition, especially by the advocates of the so-called hydrate theory, according to which the act of solution involves a more or less intimate or structural union of each molecule of the solute with one or more molecules of water. The trend of opinion at present is toward some form of the hydrate theory, but it does not seem to have been noticed, except by Tammann,¹ that certain properties of solutions are demonstrative against the theory of free solute and inactive solvent, and in favor of the theory that there exists such an interaction between the solute and the solvent that certain properties of the solvent are modified thereby. As the evidence which we have does not go so far as to prove the existence of true hydrates in all solutions, and indeed is rather unfavorable to the hydrate theory, as strictly construed, I prefer to call the theory based upon it the association theory of solutions.

The evidence which proves an efficient interaction between the solute and solvent, and a modification of the properties of the solvent, was discovered by Julius Thomsen.² On investigating the heat capacities of many aqueous solutions of electrolytes, Thomsen found that the apparent heat capacity of the solute (that is, the difference between the heat capacity of the solution and that of the

¹ *Zeits. für phys. Chem.*, Vol. 18, p. 625, 1895.

² "Thermod. Untersuchungen," Vol. 1; *Wied. Ann.*, 142, p. 337, 1871.

water which enters into it) becomes less as the dilution increases, and in most cases even attains a negative value, so that the heat capacity of a dilute solution is less than that of the water which enters into it. It is manifestly inadmissible to ascribe a negative heat capacity to the solute or to any part of it. It is further impossible to account for the diminished heat capacity by ascribing it to a change in the extent of dissociation due to the rise of temperature during the determination of the heat capacity, for this change has been proved to be so small as to be negligible in this connection. We are therefore forced to believe that the solute, or some part of it, interacts with the surrounding water in such a way as to diminish the heat capacity of the water.

Thomsen also found that the apparent volume of the solute (that is, the difference between the volume of the solution and that of the water which enters into it) becomes less as the dilution increases, and in a very few cases even attains a negative value. In these cases the volume of the solution is less than that of the water which enters into it. It is manifestly impossible to ascribe this result to the shrinking of the solute alone, or to an insertion of the dissociated ions in the interstices between the molecules of water. A similar inference follows to that already drawn from the behavior of the heat capacities, that the solute, or some part of it, interacts with the surrounding water in such a way as to diminish the volume of the water.

We are thus naturally led to speculate on the mode of interaction between the solvent and the solute. Tammann assumes that the effect of the solute extends throughout the solution, so as to produce an interior pressure in it, by reason of which the heat capacity of the solution is altered. He undertakes to calculate the amount of the change by the aid of a thermodynamic formula for the specific heat, involving the specific heat of the solvent under a pressure equal to the assumed interior pressure and a correction term containing the temperature coefficients of volume and pressure. Owing possibly to the difficulty of obtaining accurate data for the necessary calculations, the agreement of Tammann's calculated values with those obtained by observation is not good, though the general course of the observations is fairly well represented.

Jones¹ and his fellow workers have been led by their observations of abnormally great freezing point depressions in concentrated solutions to adopt the view that the solute interacts with the water to form groups of molecules which are so closely bound together that they move as one body in the solution. Jones calls these combinations hydrates. He explains the abnormality of the freezing point depressions by the hypothesis that the molecules of water which combine to form the hydrates are removed from the solvent so that it contains fewer free molecules or becomes more concentrated than would be inferred from the way in which the solution is made up. By following out this hypothesis he reaches the conclusion that the extent of hydration is a function of the concentration, being generally greater as the concentration increases, at least up to a certain limit.

According to our ordinary conception of the range of molecular force, we should not expect such a variable hydration as is assumed by Jones. We should expect, rather, a practically uniform action of the molecules and ions of the solute, forming groups of water molecules which are constantly the same for all concentrations; at least for those in which the groups do not frequently interpenetrate each other.

In constructing the formulas to represent the heat capacity and the volumes of solutions, I have adopted the simple conception which has just been stated. I assume that each undissociated molecule of the solute and each ion of the dissociated molecules interacts with the water around it in such a way as to change its heat capacity and its volume; these changes being the same for all concentrations to which the formulas apply. The solution, then, is considered as a mass of free and unaffected water, in which are suspended groups of water molecules, surrounding the molecules and ions of the solute, and with their properties modified by the action of the solute. It is not necessary to consider these groups as stable. Indeed it is almost necessary, if we are to account for the laws of electrolytic conduction in harmony with this hypothesis, to consider them as extremely loose and unstable aggregations,

¹ *Zeitschrift für phys. Chem.*, XLVI., p. 244, 1903; XLIX., 385, 1904.

from which water molecules are continually breaking off to be replaced by others, and through which the ions of the solute may move without dragging with them a load of water molecules. Whether the effect of the molecules and ions of the solute is to increase or diminish the heat capacity or the volume of the water in these groups, or to leave these properties unchanged, is to be determined from the values of the constants of the formulas found for each particular solute.

It should be stated that the solutions to which the formulas have been applied are made up by dissolving one gram-molecule of the solute in N gram-molecules of water. The number of undissociated molecules and the number of the dissociated ions are then expressed as fractions. They are obtained for each solution in the usual manner from Kohlrausch's tables of molecular conductivities.

The formula for the heat capacity formed on this hypothesis reduces to the sum of three terms, of which the first represents the heat capacity of the water used in making up the solution, the second is a constant multiplied by the number of undissociated molecules of the solute, the third, a constant multiplied by the number of dissociated molecules of the solute. The two constants represent the heat capacity of the molecules and ions of the solute respectively, together with the changes which they produce in the heat capacity of the groups of water molecules associated with them.

The formula for the volume assumes the same form, and, *mutatis mutandis*, the interpretation of the constants is the same as that which has just been given.

For solutions of non-electrolytes, in which there is no dissociation, the formula reduces in each case to the sum of two terms, one of which represents the heat capacity or the volume of the water used in making up the solution, and the other is a constant which depends upon the particular solute employed.

These formulas are abundantly verified by comparison with the results of observation. With regard to the non-electrolytes it has been shown¹ that the heat capacity of their solutions, in most cases, is the sum of the heat capacity of the water and of a constant characteristic of the solute. This constant in general is not the

¹ Magie, *Phys. Review*, Vols. IX., XIII.

same as the heat capacity of the solid solute. A similar rule has been shown to hold for the volumes of aqueous solutions of cane sugar by Wade and by Wanklyn, and examples of its applicability to solutions of other non-electrolytes can be obtained by simple calculations from the data given in the tables of specific gravities. The few cases in which this rule does not hold good, notably those of aqueous solutions of the alcohols, may fairly be considered as exceptions which perhaps cannot now be explained, but which we may expect to explain in harmony with our main hypothesis.

With regard to the electrolytes, the observations of Thomsen and other observations made in the physical laboratory at Princeton by Mr. R. E. Trone, can be represented by the formulas with great accuracy and completeness. As I expect soon to publish (in the *Physical Review*) an extended comparison of the data of observation with the numbers calculated from the assumed formulas, I shall content myself here with giving a few typical examples.

The formulas to be illustrated are:

$$\text{For the heat capacity} \quad H = W + A(1 - p) + Cp,$$

$$\text{For the volume} \quad V = U + D(1 - p) + Fp,$$

in which W and U are respectively the heat capacity and the volume of the water used in making up the solution, and p is the dissociation factor, or the number of dissociated molecules of the solute, expressed as a fraction. In the tables N represents the number of gram-molecules of water in which one gram-molecule of solute is dissolved.

The constants C and F express, for the heat capacity and the volume respectively, the effect of both ions of the dissociated molecule. Either one of them may be considered as the sum of two similar constants, each expressing the effect of one of the two ions. If, therefore, we consider solutions of two binary electrolytes, each containing a common ion, the difference between their values of C or of F should be independent of the effect of the common ion, and so should be the same for the same pair of other ions, whatever may be the common ion with which they are connected. This conclusion from the hypothesis is illustrated by the sodium and

potassium chlorides, hydrates and nitrates, for which the differences of the values of C are 22, 17, 22, and of F are 8, 9, 11.5. It is not found to hold generally true when the barium and strontium chlorides and nitrates are compared with sodium chloride and nitrate. In these cases, I am informed by Professor Hulett, there are reasons to believe that there is a double dissociation of the barium and strontium salts; in which case an agreement could not be expected.

KCl, $A = 96$, $C = -53$; $D = 47$, $F = 22$.

N	ρ	H M.	H Calc.	V Th.	V Calc.
15	0.672			300.4	300.2
30	.728			569.0	568.8
50	.753	880.7	882.0	928.2	928.2
150	.787	1777.6	1777.2	1827.3	1827.3
200	.818	3571.8	3572.2	3625.0	3626.0
300	.835	5370.2	5370.2		
400	.848	7167.1	7168.1		

NaNO₃, $A = 55$, $C = -20$; $D = 37.5$, $F = 24$.

N	ρ	H Tr.	H Calc.	V Th.	V Calc.
10	0.34			212.5	213
25	.514			480.4	480.7
50	.618	908.2	908.6	929.2	929.2
100	.698	1802.7	1802.7	1828.2	1828.2
200	.757	3598	3598.2	3627.0	3627.5
300	.785	5396	5396.1		

NH₄Cl, $A = 39$, $C = -23.1$; $D = 43.5$, $F = 36$.

N	ρ	H Th.	H Calc.	V Th.	V Calc.
10	0.593	181.6	182	219.0	219.1
25	.703	443.6	445	488.2	488.2
50	.742	893	893	937.8	937.9
100	.777	1791	1791	1837.7	1837.7
200	.806	3588	3589	3637.6	3637.5

The constant C expresses the heat capacity of the ions added to the loss of heat capacity (considered therefore as a negative quantity) of the water associated with them. The negative number obtained by adding C , which is always negative, to the negative value of the heat capacity of the ions should express the loss of heat capacity of the water associated with the ions. If we use for the heat capacity of the ions the heat capacity of the molecule com-

posed of them in the solid state, or, if this is not known, make up a heat capacity for them by adding their atomic heats, as determined by Kopp, we find that the numbers obtained, with two exceptions, fall into two groups. For one of these groups, derived from the constants for sodium chloride, hydrate, and nitrate, ammonium chloride, and hydrochloric acid, the mean number obtained is —44.8, with a maximum deviation of less than five per cent. For the other group, derived from the constants for potassium chloride, hydrate, and nitrate, barium and strontium chloride, and barium nitrate, the mean number obtained is —65.7, with a maximum deviation of less than five per cent. We may conclude from these results that the effect of ions of different sorts in diminishing the heat capacity of the water associated with them is in many cases practically the same, but that other ions may exert on the water a very different effect. The presence in one group of all the sodium salts and in the other of all the potassium salts is especially significant of this last conclusion. The differences between the effects of the ions may be represented by supposing that the action of one sort extends only so far as to affect the water molecules immediately contiguous to them, while that of the other sort extends further into the water.

It is unfortunately impossible to test the formula for heat capacity in the region of extreme dilution, but the formula for the volume has been applied to Kohlrausch and Hallwach's determinations of the specific gravity of very dilute solutions in some cases and found to hold with the constants determined from Thomsen's observations at higher concentrations. In the region of high concentration the formulas sometimes fail to reproduce the observations. This can be ascribed, I believe, to the frequent interpenetration of the groups of water molecules which are associated with each molecule or ion of the solute; or, what amounts to the same thing, to the frequent action of two or more molecules or ions of solute on the same set of water molecules.

I would explain in the same way the apparent change in the extent of hydration calculated by Jones and others from the abnormal depression of the freezing points of concentrated solutions.

The hypothesis developed in this paper does not preclude a kinetic explanation of osmotic pressure. This has been shown recently by Lowry¹ and the argument does not need to be repeated here.

The representation of the molecular conductivity as a sum of two ionic velocities, according to the theory of Kohlrausch, seems to be inconsistent with the assumption of any such action between the ions and the water as will form stable hydrates, at least if the only free electric charges present in the groups constituting the hydrates are those belonging to the ions of the solute. If, however, we assume, as has been done in this paper, that the action of the ions does not form stable groups of water molecules, but only such associations of them that the ion can pass through the water without dragging a group of water molecules with it, we can then use this hypothesis without modifying the commonly accepted explanation of electrolytic conduction.

PRINCETON, N. J., April 19, 1907.

¹ *Phil. Mag.*, April, 1907.